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13. ABSTRACT (Maximum 200 words) Thin films are used in numerous applications including optics, electronics and surface protection. Physical vapor deposition (PVD) is the commonly used method to produce thin film coatings. Standard PVD techniques produce films with inherent weaknesses in optical and mechanical properties because of their typical columnar microstructure. This structure is a result of the low mobility of the condensed atoms or molecules on the substrate surface. This is particularly true for coating of plastics, where the substrate temperature needs to be kept low (around ambient). Reactive Ion Plating Deposition (RIPD) is an innovative technique which densifies the growing thin film by enhanced surface mobility as well as by continuous ion bombardment. This results in durable well adhering thin films at relatively low substrate temperatures. This technique and other hybrid ion enhancement processes will be investigated and directed toward production-oriented applications. Further refinement of the RIPD technique evaluated in the Phase I effort will be performed.				
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FOREWORD

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INTRODUCTION

Today's modern integrated battlefield exposes ground troops to laser emissions either from hostile forces or inadvertently from friendly forces from both the ground and aircraft. These emissions can originate from laser designators, range finders, or other laser systems that have visible or infrared emissions of sufficient energy to result in temporary or permanent visual loss. Laser Eye Protection (LEP) as well as ballistic eye protection is therefore a requisite for today's ground troops. In order to achieve this dual protection, many Government programs are being directed toward the development of a combat spectacle that provides multiline laser emission protection and protection from physical impact of fragmentation exposure during battlefield action.

The current technologies used to provide "Laser Eye Protection" (LEP) are thin film multilayer reflective rejection filters, absorption filters and holographic filters. Each of these approaches has their good and bad points. The multilayer rejection filters have been used with limited success on polycarbonate surfaces. Their limitation is related to the film structure of the deposited films as well as the uniformity of the coating on curved shapes. This limitation affects both the durability and the optical properties of the deposited multilayer. Their major benefit is the high optical transmittance that can be achieved without any significant absorption characteristics. The absorbing type filters have very limited use because of their broad band rejection properties. This severely affects the scotopic/photopic transmittance as well as the field color neutrality. Absorption type filters can be used for rejecting spectral regions outside the visible spectrum as long as there are no significant visible absorption properties. The holographic filters have very good optical characteristics, but have high susceptibility to thermal effects and must be protected with a cover plate due to their poor durability.

One key problem associated with the standard Electron Beam (EB) Deposition process used for multilayer coatings, is the film porosity. Electron microscope investigations of fractured edges of thin films revealed that many metals and most dielectrics form thin films with a columnar microstructure. A major research and development thrust in various areas of thin film applications, including electronics, optics and surface protection, is geared towards the densification and homogenization of the microstructure of thin films, in order to make them "bulklike". Numerous researchers have spent their efforts in improving abrasion and erosion resistance by way of densifying the thin film microstructure. Most of these efforts had some limited success. In particular, deposition of thin films on substrates at relatively low temperatures (room temperature or moderately above) is one of the limitations for many processes. Lack of versatility for either the thin material selection or substrate size or shape is another.

The technology approach chosen for this Phase II effort is a relatively new process called reactive low voltage Ion plating (RLVIP). RLVIP appeared as a versatile method of producing hard thin film coatings with bulk-like properties for a variety of chemical compounds. These include nitrides and carbides for metallurgical application, and oxides for optical coatings. While ion-plating deposition of metallurgical coatings may still employ substrate temperatures of 400 to 500 degrees C, RLVIP of oxide coatings operates at about 100 degrees C. The capability of depositing dense, hard oxide thin or thick films at such a low temperature is advantageous for all applications where the substrate does not allow for the typical temperatures of 300 to 500 degrees C used with other EB processes. Therefore, it is anticipated that RLVIP is fully compatible with most optical materials, including classes with a low softening point.

This Phase II effort is directed toward demonstrating that this process can be used to deposit reflection rejection coatings on polycarbonate material. The significance of providing multilayer rejection coatings on polycarbonate material, using the RLVIP process, is that uniform, durable and optically efficient LEP eye wear will be possible at high production levels. A hybrid approach of using optically efficient polycarbonate IR absorbers with the multilayer coatings will provide ballistic protection and multiline LEP for the visible and NIR spectral region. The significance of using a coating process with ion interaction compared to normal deposition processes is the enhanced durability and optical stability due to bulk-like structural properties of the deposited coatings.

The primary goal of this program is to use "state of the art" technologies and materials to achieve a quantum leap in the performance of LEP hardware. The approach proposed is a combination of the most advanced polycarbonate IR absorbing materials, for a base ophthalmic element, and a novel multilayer reflection rejection filter applied to the polycarbonate material. Glendale Protective Technologies, Inc. provided the polycarbonate near IR absorbers with specific ophthalmic shapes.

Evaporated Coatings, Inc. and the Center for Research in Electro-Optics and Lasers(CREOL) at the University of Central Florida(UCF) agreed to provide a cooperative effort for studies related to depositing multilayer coatings on polycarbonate materials. CREOL has established a major program in the fundamental and applied research for a substantial improvement of thin film coatings for optical applications. The coating technology that will be used by CREOL is RLVIP, which is considered a major breakthrough in thin film deposition technology. It is anticipated that this technology can be used to enhance not only the optical properties of multilayer coatings on polycarbonate but also the coating durability and coating uniformity properties.

Evaporated Coatings, Inc. (ECI) primary effort is to provide complementary technical studies such as: studying transitional layer(s) that enhance the adhesion between the multilayers and the polycarbonate substrates, providing absorbing polycarbonate substrates that complement the multilayer reflective coating designs, and evaluating the optical, physical and environmental properties of both the CREOL and ECI coatings. As a secondary effort, ECI will be studying their High Density Plasma(HDP) deposition process to determine the feasibility of using this process for the high volume deposition of LEP coatings on polycarbonate substrates.

ECI STUDIES

ECI's objective is to complement CREOL's work in providing a durable dielectric multilayer reflective rejection coating on a selective absorbing polycarbonate(PC) lens that can provide both laser eye protection (LEP) and ballistic eye protection (BEP). The spectral regions of interest for LEP are the far visible and near infrared. The specific areas that will be addressed are:

- A. Feasibility of using ECI's HDP process as a complement or alternative to CREOL's RLVIP process.
- B. Investigate transitional layers as an interface to the soft polycarbonate substrate and hard dielectric multilayer coating.
- C. Hybrid HDP/RLVIP coatings on Polycarbonate material.
- D. Physical, optical and environmental evaluation of ECI and CREOL coatings.
- E. Absorbing polycarbonate ophthalmic lenses.

A. Feasibility of Using ECI's HDP Process as a Complement or Alternative to CREOL's RLVIP Process.

Simply, the HDP system utilizes a high power plasma discharge to deposit material to a substrate as a very dense film. Argon, the most commonly used gas, is introduced into the chamber to provide a medium for the discharge where gas pressures can range from a few mtorr to approximately 100 mtorr. We feel the HDP process is well suited for polycarbonate materials, where substrate temperature is critical. It is this temperature that can influence both the optical and physical characteristics of a deposited film on a soft polycarbonate substrate. As a comparison, most electron beam systems need substrate temperatures in a range of 300C to 500C for optimum hard coatings. In the HDP process, substrate

temperature can be controlled by not only varying power, but time of deposition, gas pressure and mixture (i.e., the addition of oxygen). In addition to controlling substrate temperature the system does contain a chilled water platen station to dissipate heat from a substrate during deposition.

Our initial studies centered on establishing deposition parameters for high refractive index materials tantalum pentoxide (Ta_2O_5) and niobium pentoxide (Nb_2O_5) as well as a low index material silicon dioxide (SiO_2). They were considered because of our previous experience of using these films on glass substrates. The film's mechanical (i.e., adhesion, durability, environmental) and optical properties (i.e., refractive index, absorption) have some very desirable properties.

Initial deposition parameters (i.e., power, time, gas pressure) were taken from data used on some previous runs not associated with this project. We first deposited these films on 1 X 3 glass substrates to establish uniformity for each of the materials. Optical measurements were used to determine deposition rates and tape tests (MIL-M-13508) were conducted to test film adhesion.

Film adhesion proved not to be reproducible during our initial test runs on PC substrates. A possible cause of this was our standard soap/water cleaning procedure. Modifications to our standard cleaning procedure did not improve quality and/or adhesion, until we subjected the substrates' surface to a sputter etch after cleaning. The HDP system allows us to sputter etch and deposit in the same pump down. With this etch process, we can remove a layer of "contaminated" PC and at the same time heat the surface enough to remove water absorbed by the PC material. A new aluminum lens holder was made to dissipate as much heat away from the substrate as possible during the deposition. To do this the fixture was matched to the lens' curvature and to the flat surface of the platen.

For test purposes we used clear polycarbonate substrates with and without a hard organic coating. The coating (applied by the manufacturer) is designed to protect the soft polycarbonate surface from external damage. Also, the organic coating could possibly act as a transitional interface for the deposited hard dielectric multilayer coating and the soft polycarbonate surface. Finally we could use it as a hard protective coating for the overall hybrid array.

A test matrix was designed (SEE TABLE 1) to compare clear uncoated(CUC) and clear coated(CC) PC substrates by depositing single layers of Ta_2O_5 , Nb_2O_5 , and SiO_2 on each. In addition, we compared substrates with and without sputter etching. Tape tests were conducted on the samples immediately after being coated and were subjected to an environmental (immersion in $\text{D}_2\text{H}_2\text{O}$) stress test for a specified time. Results show all CC PC substrates to pass environmental testing, but cosmetically the films looked blotchy in appearance.

The one CUC lens that passed, had excellent color and clarity. Because of this we pursued using the clear uncoated substrates further. Another test matrix (SEE TABLE 2) was designed to optimize the sputter etching parameters on CUC PC lenses. Substrates were sputter etched in an argon plasma with and without oxygen for two power levels (100W and 200W) for the same time. Oxygen was introduced during the sputter etch procedure to see what affect, if any, it would have on improving the adhesion. We picked Nb₂O₅ because we had not tested it as much as was previously done with Ta₂O₅. Three substrates failed adhesion immediately after deposition, and the remaining two passed environmental stress. Of the two, one lens had been prepared with a prebake in another vacuum system. This approach could be a possible addition and or alternative to sputter etch processes. Since the sputter etch process could be done in the same system without breaking vacuum, and based on the final test results, we incorporated the sputter etch process into our deposition procedure.

Our next phase of the study was to optimize deposition parameters (i.e., power, time, gas mixtures) previously established, while maintaining a minimum substrate temperature that is critical to the process. We will then analyze the resulting data of the film's optical(absorption) and mechanical properties(adhesion) to secure final deposition parameters.

Substrate temperature must be controlled in order for films to adhere well to a polycarbonate substrate. If the temperature gets too high, the substrate will swell and outgas, and the deposited film, because of its own compressive stress, will delaminate or be under considerable stress once the substrate temperature begins to cool. A test matrix (SEE TABLE 3) was setup where power, time, and gas mixtures (argon to oxygen ratio) were varied while monitoring substrate temperature. Based on previous results, we continued with clear uncoated(CUC) PC substrates, using the same aluminum lens cooling fixture previously mentioned. Specifically, we discovered we could reduce the oxygen to less than 2.0% for the same power levels of high index material and keep the substrate temperature to less than 80C. The deposition rate for Ta₂O₅ was almost twice as fast as Nb₂O₅ for the same deposition parameters. Substrate temperature, however, was 10 degrees higher for the Ta₂O₅ than the Nb₂O₅ deposition. Both still fell within the maximum tolerable limit of 80C. Adhesion failed for Ta₂O₅ and Nb₂O₅ when oxygen levels were above 5.0%. Because of the fixturing and the type of source we used to deposit the SiO₂, substrate temperature far exceeded design limitations. The SiO₂ was deposited in 100% argon, and it became evident from the first run that we had to decrease the power. Reducing the power did not reduce the substrate temperature significantly. We increased the substrate to source distance and the temperature dropped to well within design limits for the same power level.

Based on the discovery of how much oxygen affects both deposition rate and substrate temperature, we designed a new matrix (SEE TABLE 4) to accelerate the deposition rate and reduce substrate temperature even further. We deposited Ta₂O₅ and Nb₂O₅ as halfwave films on BK-7 glass, and from spectral measurements of transmission determined absorption losses. Oxygen levels of 1.0% reduced temperatures to a very acceptable level (60 to 65 degrees C), while absorption losses calculated for both materials were 0.1% and 0.2%. Films with oxygen levels reduced by 0.5% proved to be either very metallic or exhibited a very high absorption. We also increased power levels where both temperature and absorption exceeded our parameters at lower levels. We were able to get one low oxygen deposition, with a lower absorption for Ta₂O₅, but because of the control needed to maintain a reproducible deposition we decided to stay with a higher oxygen.

We selected materials and deposition parameters based on our final results. We selected Ta₂O₅ and SiO₂ as our high and low index materials. The Ta₂O₅ exhibited higher deposition rates than Nb₂O₅, but we will not eliminate it until we have tested both as multilayers. We decided on a 1.0% oxygen to argon ratio for the Ta₂O₅ with a power level of 300W. We selected for the SiO₂ 125W in an argon only atmosphere. Sputter etching the substrate's surface under vacuum (200W, 5 min., Ar atmos.) prior to deposition, has become a necessary part of the process. We are able to remove "contaminated" materials as well heat the surface to remove absorbed water.

B. Transitional Layers as an Interface To The Soft Polycarbonate Substrate and Hard Dielectric Multilayer Coating.

Matching the expansion coefficient and the chemistry of both the hard inorganic multilayer coating and the soft organic polycarbonate substrate has been a problem in the coating industry for some time. The expansion coefficients of plastics are significantly higher than that of the inorganic coating materials. During the coating process, if there is any significant increase in the temperature of the plastic substrate, the plastic will expand more than the coating. Upon cool down, a stress will develop at the substrate/coating interface that is proportional to the process temperature change. Further, if there is not a good bond between the coating and the substrate, the coating will delaminate due to the interfacial stress caused by temperature or environmental changes. Basically, what is needed is an interfacial layer that can accommodate for the expansion coefficient differences as well as the adhesion properties of each interfacial material. ECI's technological approach is to evaluate and select a thin film to act as a "quasi" organic/inorganic transitional layer at the interface. One approach was to introduce the organic methane(CH₄) to the plasma during deposition of the Ta₂O₅, Nb₂O₅ and the SiO₂ material to create this complex compound interfacial layer. Another

approach was to use our HDP process to create a diamond like carbon coating to act as the interfacial layer.

Our studies at this time were to develop a set of process parameters using our current selected materials (Nb_2O_5 , Ta_2O_5 , SiO_2) with a plasma containing methane(CH_4). Our first study centered on a process matrix (SEE TABLE 5) to vary concentrations of CH_4 for glass substrates to determine what affect they would have on the refractive index of each material. Concentrations of 2.5% and 5% CH_4 with approximately 3% oxygen and the balance argon were selected as a starting point. Initial depositions for each high index material were made without CH_4 to first establish a baseline. We did test the SiO_2 at this time without the CH_4 to see if our measurements and calculations to get refractive indexes were correct. We calculated refractive indices from measured spectral data and found indices to be within each of the films' specifications. The films did not exhibit any type of absorption and initial adhesion tests proved positive. Included with each deposition was a No.1 25mm sq. cover glass. The thin glass was coated to see what stress if any might exist in any of the films with or without CH_4 . Films looked clear and hard on the thin glass as did the 1X3 slides. Under macroscopic examination, using normal light through a cross polarizer, there were no signs of stress evident for the thin glass. On our second study on transitional layers, we set up another matrix (SEE TABLE 6) to evaluate clear uncoated(CUC) lenses for the same deposition parameters previously used for glass. Oxygen levels were set at 3.0% and methane levels were set to 5.0% and 10.0%. Substrate temperature levels remained within specification but adhesion failed, for all films with CH_4 , immediately following deposition. Again the films were clear and hard as before without any indication of losses from absorption. An adjustment was made on the oxygen level from 3% to 1%. Both high index coatings formed by this process had excellent adhesion properties. On the basis of the positive results using a reduced oxygen in a CH_4/AR mixture, we coated both CUC and CC PC substrates with and without the presence of CH_4 .

All samples were subjected to 24 and 72 Hr. environmental stress and all passed except one substrate (CUC/ Ta_2O_5 with CH_4) which failed after 24 hrs. We split the lot and delivered the first half to CREOL to deposit an 18 layer stack at 800nm using their E-beam and RLVIP process. ECI received the coated substrates back from CREOL with their multilayer added and initial evaluation of these parts indicated adhesion failure. The remaining balance of substrates was sent to CREOL for the same processing and returned to ECI. The coatings were delaminating as received by ECI and all failed adhesion when tape tested.

Our next study of transitional layers centered on developing a diamond like coating(DLC) utilizing our smaller HDP system. DLC coatings could possibly act as both a transitional layer and a hard protective coating to complete arrays. We used a pure carbon source with a 20.0% methane introduced into an argon plasma.

Substrates were not sputter etched and deposited films were optically monitored for quarterwaves at 800nm. Adhesion was excellent and the film was clear and uniform. Some of these samples were sent to CREOL with the samples mentioned in the previous paragraph. An 18 layer RLVIP stack was deposited with the methane treated samples. The results, coating delamination, were the same as the methane treated samples. No further studies were done on the DLC coatings.

The HDP deposited transitional layers held up well after environmental exposure, but failed when overcoated with the RLVIP multilayer stacks. The thermal levels of the HDP process were kept low, but it is believed that the high process temperatures of the RLVIP process are sufficient to generate thermal stresses that are significantly higher than the adhesive benefits of the transitional layers.

C. Hybrid HDP/RLVIP Coatings on Polycarbonate Material.

Our approach for this study is to use the deposition parameters established from previous test results (based on single layer coatings) to deposit HDP multilayer coatings on PC lenses. The films will be evaluated for their film quality, reproducibility, and environmental stress. Also, we will attempt to overcoat the RLVIP coatings with our HDP multilayer stacks. CREOL, in turn will overcoat our HDP coatings with their RLVIP coatings. Final results from this study will determine ECI's direction and implementation for a final process to complement CREOL's RLVIP process.

Several attempts were made to deposit 2, 4, and 8-pair HDP stacks of Ta₂O₅/SiO₂. Most evident during the depositions was the high substrate temperature (>90C) during the SiO₂ deposition. We believe this was the main reason for film failure before and after environmental stress. After we made some geometrical changes, we were able to keep the temperature to within design limits during the deposition. An 8-pair stack (Ta₂O₅/SiO₂) was then deposited on a CUC PC substrate (peaked at 800nm) after incorporating the new geometry. The part was subjected to environmental testing and passed. We repeated the run, depositing on two dyed absorber lenses, 16 and 32-pair stacks respectively. The 32-pair stack had only minor film damage after 14 days of environmental and the 16-pair stack survived a six(6) day exposure. Final results show we can deposit well adhering and stable stacks to polycarbonate substrates with the HDP process.

As part of ECI's goal to complement CREOL's work, CREOL sent polycarbonate substrates with RLVIP single layer (SiO₂, In₂O₃) and double layer (SiO₂/In₂O₃) coatings. CREOL deposited In₂O₃ using their RLVIP process and their E-beam process for the SiO₂. We deposited an 8-pair stack(Ta₂O₅/SiO₂) onto each sample. Failure occurred for all samples except one single layer of EB

deposited SiO₂. Since the SiO₂ sample provided by CREOL was EB deposited and all other samples were RLVIP deposited, we believe that this is one indication of the type of failure made. The EB process has a much lower process temperature than the RLVIP process. This sample, therefore, did not exhibit damage because of the lower process temperature. A more detailed discussion of our results is described in the following evaluation section.

We investigated the possibility of depositing a stack by our E-beam process and depositing on top of that an additional 8-pair in our HDP system. We considered the soft spongy layer of an EB film as a possible interface to very compressive HDP stack and the soft polycarbonate substrate. The E-beam stack peaked at 800nm and when we completed the HDP stack on top, the completed hybrid stack shattered totally before it could even be measured. The combination of stress in the EB coating and the HDP coating yielded a high composite stress coating. No further studies were pursued because of this negative result.

D. Physical, Optical and Environmental Evaluation of ECI and CREOL Coatings.

In the initial stages of the program we received from CREOL seven PC lenses. All substrates were coated with their Reactive Low voltage Ion Plating(RLVIP) process. Four of the seven were double layers and the balance single layers as shown below;

930102A	In ₂ O ₃ + SiO ₂
930102B	In ₂ O ₃ + SiO ₂
930101A	SiO ₂
930101B	SiO ₂
930105A	SiO ₂ + In ₂ O ₃
930105B	SiO ₂ + In ₂ O ₃
921219	In ₂ O ₃

On initial inspection we found 930102A film to have a large crazed area. Lens 930102B had what looked like cleaning 'swipe marks' on its surface. All others looked good except for occasional pinholes in the coatings. Optical measurements of the coated lenses were made and indicated a wavelength peak around 850nm. Prior to environmental testing, the lenses were subjected to a tape test(MIL-M-13508) and passed. After being immersed in DiH₂O for 120hrs., they were again given a tape test. Sample 930102A failed and the remaining six did pass. No other tests were performed and they were returned to CREOL. At this stage of the studies, it appeared that single and double layer RLVIP coatings were good.

Samples were sent to CREOL that were coated from a test matrix designed by ECI to study transitional layers (see topic under transitional films) and DLC films. These coatings were subjected to our standard environmental stress and passed prior to delivery to CREOL. Macroscopic inspection by ECI after CREOL coated them showed complete film failure, including blistering, compressive fractures, pinholes and particulate damage. A second set of lenses sent to CREOL (not environmentally stressed), was processed by them the same way and failure was a repeat of the first set. It appears that the transitional layer was not beneficial for the hybrid system.

We received and evaluated for CREOL single layer (SiO_2 , In_2O_3) and double layer ($\text{SiO}_2/\text{In}_2\text{O}_3$, $\text{In}_2\text{O}_3/\text{SiO}_2$) coatings, as well as multilayer stacks that they deposited on clear coated PC substrates. Representative samples of each were subjected to environmental stress and those failed within 24Hrs. Sister samples not exposed to environmental stress were overcoated with an additional 8-pair stack by our HDP process and subsequently given environmental stress. Failure occurred for all with 24Hrs except one, and that was where the clear coated substrate had been coated with SiO_2 by CREOL's E-beam process. Throughout the CREOL studies the In_2O_3 films were deposited using the RLVIP process and the SiO_2 films were deposited with the EB process for the multilayer coatings.

A final set of lenses, coated by CREOL with their RLVIP process, were sent to ECI for evaluation. The multilayer was deposited very slowly (approximately seven days) in an attempt to keep process temperatures low enough that differences in expansion coefficients between the polycarbonate and the multilayer would not be significant. The overall appearance looked good under examination. The coatings, however, failed environmental stress testing. It is believed that the high compressive stress of the multilayer coating precipitated the failure.

Based on our evaluation of CREOL's coatings, it appears that the process cannot be used to deposit a complete dielectric stack that can survive environmental testing. Whenever the RLVIP coatings are used in multilayer stacks or hybrid stacks, the coatings failed testing. It is believed that the elevated temperatures of this process and the high compressive stress of the multilayer contribute to the failure of the coatings.

E. Absorbing Polycarbonate Ophthalmic Lenses.

Glendale Protective Technologies, Inc. provided Evaporated Coatings, Inc. with both clear and selective absorptive polycarbonate lenses. In addition, they provided lenses with an organic protective layer to enhance the durability of the soft polycarbonate material.

The joint effort of ECI and Glendale Protective Technologies was to develop a hybrid absorbing polycarbonate material with applied multilayer coatings that would be complementative. The approach was to use IR absorbers to an optimal concentration that would not significantly degrade the scotopic and photopic transmittance of the filter. The multilayer coatings could then be used to increase the optical densities of the IR laser lines. Since the multilayer coatings are non-absorbing, they do not degrade the visible transmittance. A typical spectral transmittance curve for the selected polycarbonate absorbing lens is illustrated in figure 1.

CREOL STUDIES

CREOL utilized their RLVIP process to deposit single and multilayer coatings on polycarbonate ophthalmic material. Their studies addressed hybrid RLVIP/EB multilayer coatings, thermal control of the deposition process, coating material selection, transitional layers and the evaluation of the deposited coatings.

The coating process (Reactive Low Voltage Ion Plating) and the system used by CREOL is described in detail in the SBIR Phase I final report. Basically, this mode of coating deposition uses a combination of electron beam deposition with a plasma system that ionizes the evaporated atoms/molecules from the electron beam gun source. The evaporated ions are then accelerated toward the substrates by a bias voltage. These accelerated ions increase the surface impact energy and thus the surface energy at the film/substrate or film/film interface. This provides the densification of the deposited film by increased surface mobility. The films deposited approach "bulk-material" properties compared to a columnar void structure of films formed by standard electron beam deposition technology. A caveat to the RLVIP process is that the films formed have a tendency toward forming films in compressive stress. A schematic of the Balzers BAP 800 equipment used for the CREOL studies is illustrated in figure 2.

A. Thermal Control of the Deposition Process

Studies performed by CREOL in the Phase I effort indicated that the process provided too much heat when depositing a multilayer coating on the polycarbonate substrate. The source of this heat is both the electron beam gun source and the plasma source. The heat directly impinges on the polycarbonate lens as well as indirectly from the reflections off of the chamber walls and the emissions from the chamber walls. It was reasoned that the direct heat cannot be controlled but the emissions from the walls could be controlled to some degree by heat sinks and shielding. During the Phase I studies CREOL built a heat exchange system for the coating system. This did reduce process temperatures considerably but temperatures were still higher than desirable for depositing coatings on polycarbonate. Additional heat sinks and shielding were added for the Phase II effort. The increased cooling capacity allowed for marginal use of the reactive ion plating process. However, extended deposition times (more layers) were not possible because of substrate temperature increases beyond acceptable levels. Cool down times were required to maintain lower process temperatures. Although the chamber walls thermal emissions are controlled to a significant degree, it appears that the direct emissions from the e-gun source and plasma are enough to keep the process, at best, marginal.

B. Coating Material Selection

Coating material selection is based on design requirement properties (refractive index and absorption constant), physical and environmental properties, deposition techniques, compatibility with polycarbonate material and thermal emission properties during film deposition.

Several coating materials were evaluated during the Phase I studies. To satisfy the design requirements for a multilayer coating, a binary combination of coating materials is normally needed. The materials selected from the Phase I studies were zirconium oxide for the high refractive index material and silicon dioxide for the low refractive index material. The zirconium oxide material being a very high melting point material (2700 degrees C) generates a significant amount of heat during the deposition process. Even with the Phase II upgrade of the heat sink, the substrate temperatures of the polycarbonate substrate reached the deformation temperature of the plastic during the deposition of the zirconium oxide material. CREOL searched for another material to use as a substitute for the zirconium oxide material, a material that has some appealing characteristics (high index, good durability, and a lower melting point: 700 degrees C). The material selected for further evaluation was indium oxide. It was hoped that because of the lower temperature deposition properties that this material, in combination with

silicon dioxide, could be used to form the multilayers on the polycarbonate substrates.

Temperatures were reduced using the indium oxide material but still exceeded acceptable levels for the polycarbonate substrate material. Incremental deposition techniques were required to keep temperatures at marginal levels. It is believed that the temperatures generated by the plasma adds a considerable thermal load to the coating process.

Since it is believed that the indium oxide material still had the best thermal deposition properties, this material and the silicon dioxide material were selected for future multilayer deposition studies.

C. Transitional Layer

Because there is a substantial difference (chemistry, hardness, expansive coefficient, etc.) between the polycarbonate substrate and the multilayer reflective coating that is deposited on the substrate, the coating adherence and durability characteristics are normally degraded. In order to improve these properties, a transitional layer is placed between the substrate/multilayer coating interface.

Evaporated Coatings studied this problem and their studies and results are addressed in another section of this report. CREOL, however, did study the adhesion differences between polycarbonate lenses coated with a protective hard "organic" coating and lenses without that coating. The results for their deposition process were that the polycarbonate lenses with the hard coating were better than the uncoated polycarbonate lenses. Because of the added benefit with the hard coat, CREOL utilized the hard coated lenses for the remaining studies.

Both CREOL and ECI provided each other with lenses coated with a transitional layer using their respective coating processes (HDP and RLVIP). CREOL and ECI then deposited multilayer coatings on each of the samples. The results are addressed in another section, but basically it is believed that the coatings using the RLVIP process created high coating stress due to the excessive thermal deposition load.

D. Hybrid RLVIP/EB Multilayer Coatings

The results of the initial single layer studies indicated that the heat generated would prohibit all the films of the multilayer stack being formed by RLVIP process. The temperature of the polycarbonate substrate would approach its melting point with this process. An approach that could use both the porous properties of the EB films and the dense films formed by the RLVIP process were studied as a possible solution to limiting the process temperature and thus the induced stress of the multilayer coating. The films formed by the electron beam deposition are porous and this spongy structure may be able to adjust better to the large thermal expansion of the plastic substrate than a dense film formed by the RLVIP process. Since a plasma is not used in the EB deposition process, the process temperatures will be considerably lower. A negative to this process is the coatings are soft and porous and therefore susceptible to physical and environmental damage. These porous or spongy films also tend to be under intrinsic tensile stress. In order to compensate for the negative properties of the porous films, it was reasoned that if the normally very dense, hard and well adhering films formed by the RLVIP process were placed in key positions of the multilayer stack, they could compensate for the negative properties of the EB films. In addition, since the RLVIP films are under high compressive stress, they could compensate the tensile stress of the EB films.

A few approaches in the thin film design were tried with this hybrid system. In one case, the bottom two and top two layers were Ion plated and the intermediate films were E-beam deposited. In another case, the layers were alternated with the HDP and RLVIP process. The results of the two approaches were not very encouraging. Temperatures were again high and cool down times between the layers were long. The coatings formed were optically clear, but multilayer coatings had stress cracks to some degree. The parts that appeared to look good were subjected to physical and environmental testing. None of the coatings were able to pass this basic testing.

E. Final Report For CREOL's Studies

The final report for the studies performed at CREOL (University of Central Florida) is included as Attachment #1. Four representative samples of their RLVIP coating deposited on polycarbonate lenses were also provided as part of the completion of their project.

CONCLUSIONS/RECOMMENDATIONS

The primary purpose of this project is to determine if the Reactive Low Voltage Ion Plating (RLVIP) deposition process could be used to produce high volume laser eye protection components. Specifically, a polycarbonate lens designed with a hybrid absorptive material and coated with a RLVIP multilayer reflection rejection coating is the component studied. It is designed to provide a high scotopic and photopic transmittance and several laser line rejections in the far-visible and near-IR spectral regions. The polycarbonate material, because of its' high impact resistance, provides the ballistic eye protection.

The conclusions and recommendations based on this effort are as follows:

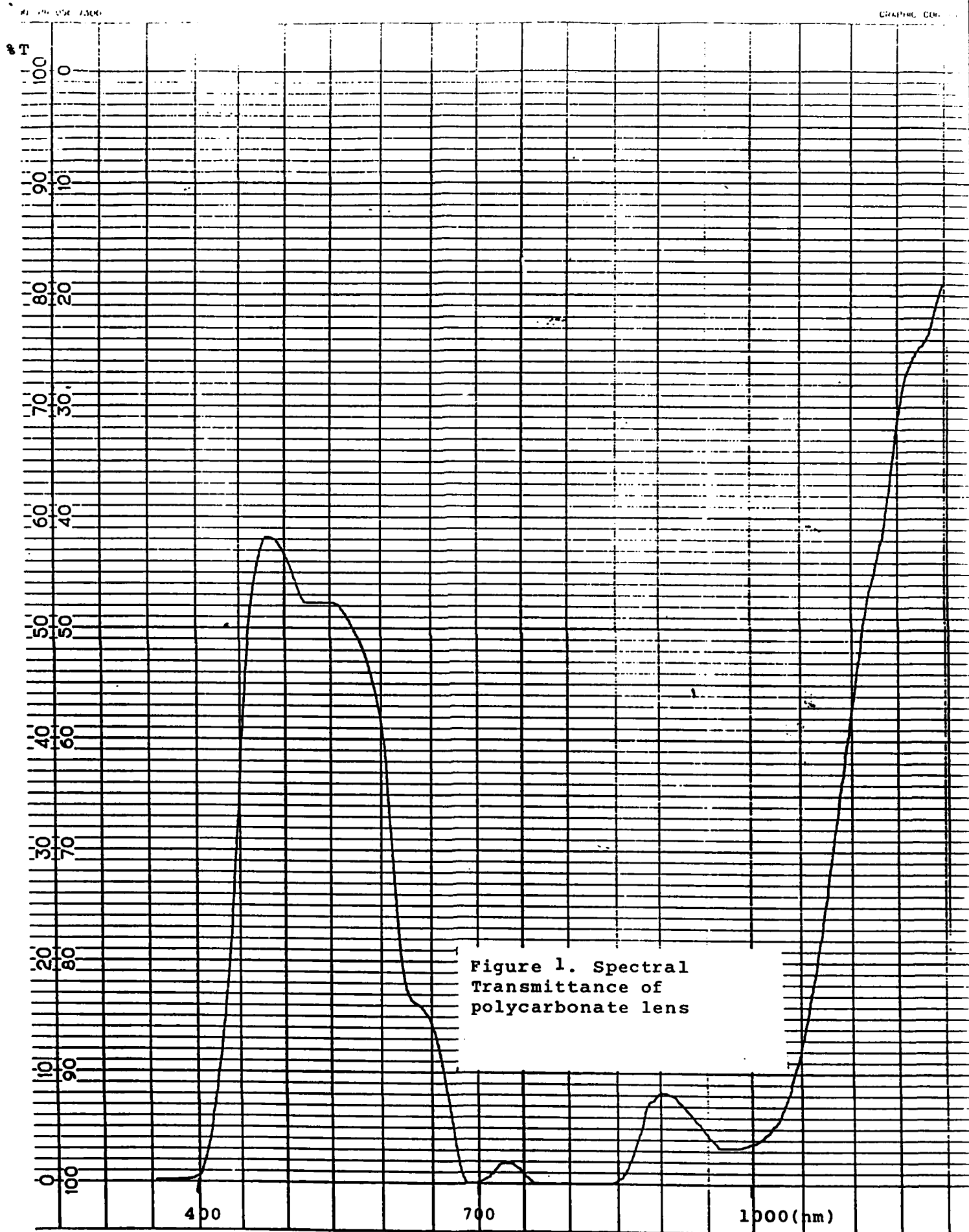
It does not appear that the RLVIP deposition process is suitable for coating low temperature materials such as polycarbonate. It may be acceptable for single or binary layers, but it is unacceptable if depositing multilayer coatings. Basically, the combination of heat from the electron beam source and the plasma produces temperatures far in excess of acceptable levels for plastics such as polycarbonate. Even with a considerable amount of shielding and heat sinks, the process temperature remained high. Because of the significant difference in expansion coefficients between the multilayer coating and the plastic lens and the process temperatures achieved, the resulting stress set up is enough to cause coating and substrate damage.

The hybrid HDP and RLVIP coatings also were unacceptable. It is believed that temperatures achieved with the RLVIP process results in the same conditions described above. Even though the adhesion characteristics between the polycarbonate substrate and the multilayer coating were improved, the stress conditions produced by the process were significantly in excess of acceptable levels.

The upscaled HDP process was able to be used to produce multilayer coating and increase production levels. The upscaled process, however, produced increased process temperatures that were in the marginal zone for coating multilayer on plastic material. More process optimization could provide lower temperatures, but it does appear that as the process is scaled up, temperatures will also increase.

It does appear that using an ion interactive process is a good approach for coating low temperature materials. This type of process provides surface energies that are required to achieve hard, durable and environmentally stable coatings. What is needed is a process where heat from the plasma or the evaporation source can be removed, thus allowing films to be deposited on substrates at a significantly lower temperature.

A recommended process for achieving this condition is to utilize an ion beam sputtering source with ion assisted deposition. This process allows the plasmas created by the ion source and the ion assisted deposition source to be confined by housings that can be cooled and thus producing a cold deposition process. The resulting process should have significantly lower process temperatures and yield durable and environmentally stable coatings because of the high surface energies produced.



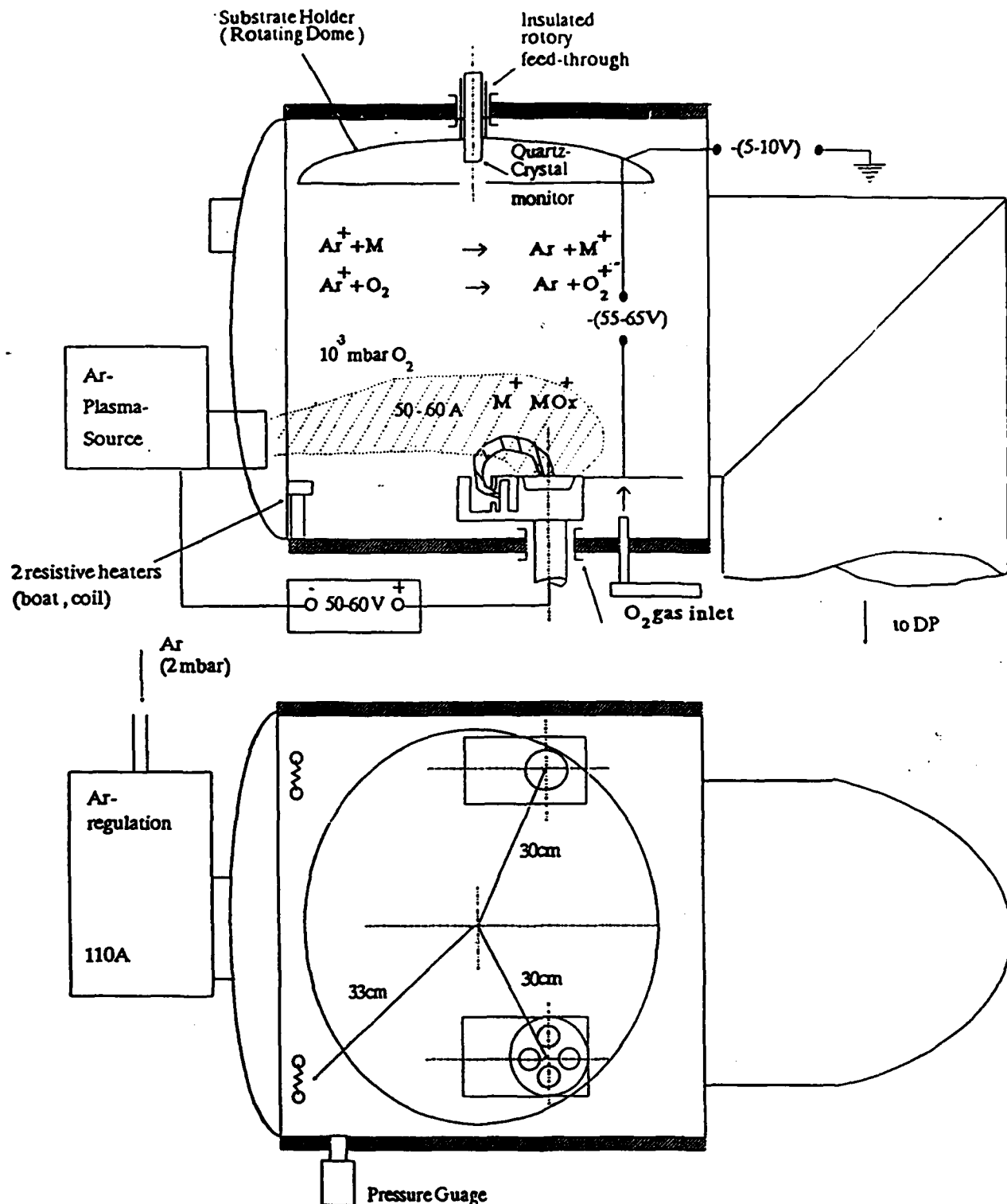


Fig. 2. Schematic of the Balzers BAP 800 equipment for reactive low voltage ion plating (RLVIP). Note the two electron beam evaporation sources in the ground view (bottom) and the low voltage, high current argon plasma source, particularly well seen in the side view (top).

TABLE ENVIRONMENTAL EVALUATION OF SINGLE LAYER COATINGS ON POLYCARBONATE MATERIAL

RUN #	SUBSTR.	SPUTTER ETCH	MATERIAL DEPOSITED			INITIAL TEST (P/F)	ENVIR #1	TEST #1 (P/F)	ENVIR #2	TEST #2 (P/F)	ENVIR #3	TEST #3 (P/F)
			Ta2O5	SiO2	Nb2O5							
921104-1	CC		X			P	X	P			X	P
921105-1	CC	X	X			P	X	P			X	P
921105-2	CUC		X			F	X	F				
921106-1	CUC	X	X			P	X	F				
921106-2	CC			X		P	X	P	X	P	X	P
921109-1	CC	X		X		P	X	P	X	P	X	P
921110-1	CUC			X		P	X	F	X	F		
921111-1	CUC	X		X		P	X	P	X	P	X	P
921111-2	CC				X	P	X	P			X	P
921112-1	CC	X			X	P	X	P			X	P
921112-2	CUC				X	P	X	F				
921113-1	CUC	X			X	P	X	F				

NOTE: CC = CLEAR COATED POLYCARBONATE LENS
 CUC = CLEAR UNCOATED POLYCARBONATE LENS
 'X' INDICATES TASK COMPLETED
 ENVIRONMENTAL #1 & #2 = 24Hr IMMERSION IN DiH2O
 ENVIRONMENTAL #3 = 120Hr IMMERSION IN DiH2O
 TAPE TESTS; INITIAL, #1, #2, and #3 MEET MIL-M-13508

TABLE 2 SPUTTER ETCH EVALUATION OF CUC POLYCARBONATE MATERIAL

RUN #	SUBSTR.	SPUTTER				VAC BAKE		INITIAL TEST (P/F)	ENVIR TEST #1	
		100W, 5'	100W, 5'	200W, 5'	200W, 5'	75 C	DEPOSIT		#1	(P/F)
		Ar ONLY	Ar + O2	Ar ONLY	Ar + O2	45'	Nb2O5			
921203-1	CUC		X				X	F	X	
921216-1	CUC				X		X	F	X	
921217-2	CUC			X			X	P	X	P
921230-1	CUC					X	X	F	X	
921231-1	CUC	X				X		P	X	P

NOTE: CUC = CLEAR UNCOATED POLYCARBONATE LENS

'X' INDICATES TASK COMPLETED

RUN# 921231-1, SPUTTER ETCH OCCURRED AFTER VAC BAKE

ENVIRONMENTAL #1 = 24 Hour soak in D:H2O

TAPE TEST MEETS MIL-M-13508

TABLE 3 POWER/DEPOSITION RATE TEST

RUN #	SUBSTR.	MATERIAL DEPOSITED	Ar	O2	POWER	TIME	TEMP.	T MEAS.	T MEAS.	DEP RATE	INITIAL
		Ta2O5 SiO2 Nb2O5	(%)	(%)	(W)	(mins.)	(C)	(nm)	(%)	(A/min.)	TEST
930419-1	CUC	X	96.4	3.6	300	40	80	800	73.6	24.0	P
930420-1	CUC	X	96.4	3.6	400	30	82	700	72.6	28.0	P
930420-2	CUC	X	98.2	1.8	300	40	80	1500	76.4	45.0	P
930420-3	CUC	X	94.7	5.3	200	40	87	800	78.0	24.0	F
930421-1	CUC	X	98.2	1.8	300	40	70	850	73.6	25.0	P
930421-2	CUC	X	87.0	5.3	300	40	84	600	72.0	18.0	F
930421-3	CUC	X	91.9	3.6	300	40	83	1170	76.8	35.0	P
930421-4	CUC	X	100.0	0.0	175	10	120	TEMP.	100	HIGH	P
930422-1	CUC	X	100.0	0.0	125	30	100	TEMP.	100	HIGH	P
930422-2	CUC	X	100.0	0.0	125	30	70	UNABLE	TO MEAS.		

NOTE:

'X' INDICATES TASK COMPLETED

CUC = Clear UnCoated PC Substrate

Substrates surfaces were pre-sputtered for 5 mins. @ 200W

"ECI CONFIDENTIAL PROPRIETARY INFORMATION"

TABLE 4
ABSORPTION TESTS

RUN #	SUBSTR.	MATERIAL DEPOSITED Ta205 SiO2 Nb205	Ar (%)	O2 (%)	POWER (W)	TIME (mins.)	TEMP. (C)	T MEAS. (nm)	T MEAS. (%)	ABSORP. (%)
930426-1	BK-7	X	99.0	1.0	300	40	65	870	91.0	N/A
930503-1	BK-7	X	99.0	1.0	300	35	62	790	91.8	0.2
930503-2	BK-7	X	99.0	1.0	300	35	71	500	90.1	N/A
930504-1	BK-7	X	99.0	1.0	300	55	62	705	91.6	0.4
930504-2	BK-7	X	99.5	0.5	300	55	65	(905)	91.9	0.1
930505-1	BK-7	X	99.5	0.5	400	35		(MIRROR)	2.0	N/A
930505-2	BK-7	X	99.0	1.0	400	25	76	801	91.1	0.9
930505-3	BK-7	X	99.0	1.0	400	35	82	695	91.6	0.4
930506-1	BK-7	X	99.5	0.5	300	30	62	1050	92.0	0.0
930506-2	BK-7	X	99.5	0.5	300	19	68	(DARK)	HIGH	ABSORP.

NOTE:

'X' INDICATES TASK COMPLETED

'T MEAS.' IS TRANSMISSION AT HALF-WAVE PEAK

'ECI' CONFIDENTIAL PROPRIETARY INFORMATION"

TABLE 5 METHANE TESTS

RUN #	SUBSTR.	MATERIAL DEPOSITED			PRESSURE			POWER	TIME
		Ta2O5	SiO2	Nb2O5	Ar	O2	CH4	(W)	(mins.)
930225-2	GLASS			X	8.2	2.5	0.0	175	60
930303-1	GLASS			X	4.2	2.6	4.5	175	60
930304-1	GLASS			X	6.0	2.5	2.5	175	60
930304-2	GLASS	X			8.0	2.5	0.0	175	60
930308-1	GLASS		X		8.0	0.0	0.0	175	60
930316-1	GLASS	X			4.5	2.4	5.5	175	60
930317-1	GLASS	X			6.2	2.5	2.4	175	60

RUN #	SUBSTR.	MATERIAL DEPOSITED			LAMBDA	R	T	n	THICK.	DEP. RATE
		Ta2O5	SiO2	Nb2O5	(nm)	(%)	(%)	(calc.)	(A)	(A/min.)
930225-2	GLASS			X	535	28.3	71.9	2.2	600	10.0
930303-1	GLASS			X	650	25.8	64.3			
930304-1	GLASS			X	705	25.3	74.9	2.2	812	13.5
930304-2	GLASS	X			746	22.6	77.1	2.1	901	15.0
930308-1	GLASS		X		777	3.1	96.0	1.469	1322	22.0
930316-1	GLASS	X			737	20.3	80.2	2.0	921	15.4
930317-1	GLASS	X			811	20.8	79.1	2.0	1004	16.7

NOTE:

'X' INDICATES TASK COMPLETED

'GLASS' IS 1 X 3 MICROSCOPE GLASS SLIDE

Argon and Methane pressure measured in mtorr

Oxygen pressure measured in 1E-4 torr

TABLE 6 METHANE(CH4) TEST ON CUC PC LENSES

RUN #	SUBSTR	MATERIAL DEPOSITED Ta2O5 SiO2 Nb2O5	Ar (%)	O2 (%)	CH4 (%)	POWER (W)	TIME (mins.)	TEMP. (C)	LAMBDA (nm)	VALUE (%)	INITIAL TEST
930405-1	CUC	X	96.7	3.0	0.0	175	60	52.0	400		
930406-1	CUC	X	96.7	3.0	0.0	200	90		1150	75.0	P
930406-2	CUC	X	96.7	3.0	0.0	200	63		750	81.5	P
930407-1	CUC	X	87.0	3.0	10.0	200	62	63.0	400		
930412-1	CUC	X	86.8	3.0	10.0	200	60	28.0	400	75.0	F
930413-1	CUC	X	86.8	3.0	5.0	200	60	31.0	975	80.0	F
930413-2	CUC	X	80.8	3.0	10.0	200	60	60.0	700		F
930414-1	CUC	X	91.8	3.0	5.0	200	60	59.0			F
930414-2	CUC	X	96.6	3.0	0.0	200	60	52.0	800	78.0	P
930415-1	CUC	X	90.0	3.0	10.0	175	60	100.0			P

NOTE: TEST #1 = 72 hr. DIH2O IMMERSION
 'X' INDICATES TASK COMPLETED
 CUC = Clear UnCoated PC Lens

ATTACHMENT NO. 1

FINAL REPORT

**Center for Research in Electro-Optics and Lasers(CREOL)
University of Central Florida
Orlando, FL 32826**

Dielectric Multilayer Laser Protection Coatings on Polycarbonate Lenses

Final Report

about Research and Development Efforts
performed as Part of a SBIR Phase II Project
at the

Center for Research in Electro-Optics and Lasers (CREOL)
University of Central Florida
Orlando, FL 32826

Period of Performance: August 1, 1991 - September 30, 1993

Magnitude of Effort (Support received): \$72,000

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October 25, 1993

CREOL/UCF Final Report to ECI on SBIR Phase II Sub-Contract Effort for R&D of
Dielectric Multilayer Laser Protection Coatings on Polycarbonate Lenses

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SUMMARY

The task of this project was, in a nutshell, to perform R&D for the prototype manufacturing of a dual laser line rejection filter consisting of a dielectric multilayer coating on dyed polycarbonate (PC) lenses. Protection against laser radiation in the near infrared (NIR) was to be provided primarily by the dye in the PC lens. The typical ruby laser line in the long red wavelength spectrum was to be rejected by a dielectric multilayer interference coating because of the steeper edge achievable, assuring higher transparency in the visible part of the spectrum (short-wave pass filter). The physical, mechanical, and thermal properties of the two classes of matter involved, dielectric inorganic thin films (oxides) and organic plastics (PC) are significantly different and do not easily match. Therefore, the process of coating of plastics¹ and the resulting coatings on plastics² have been an issue for a long time, particularly when extended durability in harsh environments is demanded, as is in field use. Problem areas encountered include the low softening temperature of plastics, the mismatch of thermal expansion coefficients (by up to a factor of 100), the difference in hardness, brittleness (or ductility), stress relaxation, and adhesion.

We attempted to produce durable multilayer interference coatings for laser eye protection on PC lenses by employing the reactive low voltage ion plating process^{3,4} (RLVIP) that had shown some promise in the Phase I work of this project,⁵ based on earlier findings of superior properties of RLVIP thin films as compared to conventional electron beam (EB) evaporated thin films.⁶ A paper presented at the 1991 SPIE Annual Meeting in San Diego reported in part on work performed in that stage of this project.⁷

The temperature rise in the coating chamber caused by the thermal load of radiation heat from the electron beam evaporation source(s) and the plasma present during RLVIP turned out to be indeed the key issue. We tried to control it by the installation of additional internal water cooled shields (over those already used in Phase I). Despite this effort, it became necessary to interrupt the coating process particularly of high refractory oxide films (ZrO_2) one or two times for each layer, what slowed the progress of our work considerably. Eventually, we decided to use In_2O_3 as the high index layer material because of the low melting point of the starting metal, the easy and complete oxidation in the RLVIP process, and better-than-average adhesion to the (organic based) hard coating

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Dielectric Multilayer Laser Protection Coatings on Polycarbonate Lenses

on the PC lenses (in comparison with other oxides). Also, some limited electrical conductivity of the (undoped) In_2O_3 thin films was thought to be advantageous in reducing electrostatic charging, both during the (plasma-based) coating process, and after (preventing excessive dust accumulation sometimes occurring with plastic lens surfaces).

Unfortunately, we were severely hampered in performing the tasks proposed for this Phase II because of

- (a) delays with another project (begun earlier) that blocked the use of the BAP 800 equipment for about 3 months longer than scheduled,
- (b) hardware problems with the BAP 800, in part probably caused by the extensive use for that other project,
- (c) change of "student labor" in the coating lab.

As a consequence, we spent a tremendous amount of time with

- (a) coating materials studies (trial runs),
- (b) equipment maintenance and service (aided several times by Balzers field service engineers, at one time being on-site for more than 2 weeks), and
- (c) additional time for start-up instructions.

These "unproductive" efforts were paid for only in part from funding received under this contract. The equipment service has been provided at no charge by Balzers High Vacuum Products, Hudson, NH, estimating their cost to be in excess of \$50,000. Some of the base work and expenditures connected with the routine operations of the coating lab were covered by funding received from the Florida High Technology and Industry Council (FHTIC) for R&D in RLVIP with Applied Research Grants in 1991 - 1993, titled "A New Class of Optical Thin Films," in the cumulative amount of about \$187,000.

We used these combined resources to investigate extensively the concept of "hybrid dielectric multilayers" (one type of thin films deposited by EBD, the other one by RLVIP) proposed for this Phase II effort. Because of the obstacles mentioned above, we had to limit our experimentation to eventually only one high index material (In_2O_3) and low index material (SiO_2). Regrettably, we were unable to meet the goal of this task to develop a process for a durable multilayer dielectric coating for laser eye protection on PC lenses that could be transferred into a prototype production stage. A final effort of

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changing from the hybrid multilayer concept to an all-RLVIP approach did not yield any significant improvement although initial test results (humidity and salt water immersion) seemed to be promising. These results, not previously reported, are contained in Appendix A.

The conclusion of this 2-years effort is, therefore, that the reactive low voltage ion plating (RLVIP) process as currently implemented in the Balzers BAP 800 is not, or only marginally, suitable for coating of plastic (PC) lenses, primarily because of the process heat generated by the plasma and the electron beam evaporation sources. The variable results in meeting optical design goals (spectral transmittance, optical density) are due to the lack of an optical film thickness monitor. The quartz crystal monitor available as the only film thickness measuring device has clearly its limitations that are probably caused by the fact that the monitoring quartz disk is on a different electrical potential than the plastic substrates, which are insulated from ground (the quartz crystal monitor is not) and accumulate electrical charges from the exposure to the plasma more easily, leading to a higher negative bias. This, in turn, is known to have a distinct influence on the film formation in the RLVIP process. Modifications of the coating equipment to change these conditions were not possible because of the high complexity both the RLVIP process itself and the integral computerized process control with manufacturer-proprietary wiring and firmware programming.

On the positive side, this project provided several students an opportunity to study thin film optics and optical coating technology in a very much hands-on manner. One of the students, Mr. Xiaofeng Han, finished the experimental part of his Master's thesis this past summer in part with work performed under this subcontract, and is now available for employment (he is a legal permanent resident). That part of his thesis dealing with his work performed for coatings on plastic lenses is enclosed as Appendix B.

TASKS AND RESULTS

To achieve optimal physical and optical properties of the compound laser protection filter proposed by ECI as the final product of this SBIR Phase II project, consisting of a dyed PC substrate and a multilayer dielectric coating, we continued our collaboration with ECI that started with the feasibility study (Phase I). We proposed to investigate the following parts of the SBIR Phase II Grant awarded to ECI:

1. Evaluation of hybrid deposition processes for dielectric thin films on polycarbonate

From preliminary results obtained with hybrid multilayers (deposited partially by EB evaporation and partially by RLVIP) in Phase I we expected that the combination of different deposition processes might give better results than any single process. In particular, we wanted to further investigate the optimum combination of electron beam evaporated and ion plated dielectric thin films, for the following reasons:⁸

Electron beam evaporation of refractory oxides (SiO_2 , TiO_2 , Ta_2O_5 , ZrO_2) produces thin films with a packing density of less than unity, i. e. there are fewer molecules per unit volume contained in the film than in a comparable slice of solid material. This packing density is a result of the low surface mobility of the evaporated atoms or molecules arriving at the surface. The surface mobility, in turn, is a function of the energy of the condensing species, which is only thermal in nature (0.1...0.2 eV). The presence of foreign molecules (adsorbates, co-deposited vapor- or gas molecules, desorbing water out of the plastic substrate) can considerably limit the surface mobility of those deliberately deposited, by occupying sites which are then inaccessible to them.

A commonly used means to increase the surface mobility of film atoms or molecules is heating the substrates to 250 - 300°C. This temperature increase provides only marginal additional thermal energy but increases the surface mobility considerably because of enhanced desorption of adsorbed gases (air molecules, water vapor) and prevention of residual gas molecules (of the same kind) present in the coating chamber from (re)adsorbing on the surface of the substrate and the growing film. Unfortunately (and

quite obviously), this common approach is unsuitable for plastic substrates which bear at most an elevated temperature of about 80 - 100°C. Hence, thermal (and electron beam) evaporation of dielectric materials, without additional process enhancement or post-deposition processing, results in rather spongy, soft films with insufficient environmental durability. The relatively large fraction of film volume not occupied by coating material (voids) causes these films to adsorb water molecules from a humid ambient environment by capillary action into the pores, or other volatile substances. Such adsorption gives rise to undesirable changes of the optical properties (spectral characteristics) of the coatings, as the initially void volume changes its refractive index from unity to that of the adsorbate (e. g. $n_{\text{water}} = 1.33$). Shifting of the spectral characteristic is undesirable in many cases, particularly if the reflection-transmission edge of a dichroic filter is close to the laser line to be rejected. Even more critical would be the shifting of a very narrow band reflection filter in the visible (for rejecting any of the laser lines in the blue-green region of the spectrum, without decreasing the photopic/scotopic transmission too much), if the resulting shift of the rejection band would bring it besides the laser line. On the positive side, the spongy structure seems to be able to adjust better to the large thermal expansion of the plastic substrate than more dense films. Also, while spongy films supposedly are soft, they can resist indentation scratching better than dense films which, though harder, are more brittle and tend to chip visibly upon indentation, if the substrate is soft (like the glazing on a chocolate cake). Porous or spongy films tend to be under intrinsic tensile stress (the molecules try to fill the voids and to assume positions more close to the bulk lattice distances). Thermally induced compressive stress as discussed below is, therefore, partially or completely compensated.

Reactive low voltage ion plating, the then fairly new deposition process pioneered at CREOL (for the U.S.) employs a low voltage high current argon plasma discharge for the continuous bombardment of the growing film with low energy ions (of 5 - 10 eV). The results are very dense, bulk-like thin films of excellent hardness and adhesion, as shown with recent micro-indentation hardness measurements.⁹ The process does not require substrate heating for enhanced surface mobility because of the substantial energy which the bombarding ions deliver to the growing film¹⁰ [for an ion-to-atom arrival rate ratio of 1:4 or 20% and an ion energy of just 5 eV, the *average* particle energy of the growing film is 1 eV, the thermal equivalent of which would be 11,000 K source temperature].

However, because of this energy delivered to the film, the energy contained in the plasma (which radiates to the substrate) and the thermal radiation of the vapor sources (electron beam evaporators), the process is not necessarily a cold one. On the contrary, the chamber temperature rises about twice as fast as for plain electron beam evaporation. The resulting temperature increase of the substrate not only would endanger plastics if going beyond the above mentioned 80 - 100°C but introduces high thermal stress at even lower temperature because of the mismatch of the thermal expansion coefficients between the thin films and the plastic substrate, which expands about 100x more. Upon cooling down to room temperature, the substrate shrinks correspondingly more than the films deposited at, say, even just 40 or 50°C, putting them under thermally induced compressive stress. Since the thin films are already under intrinsic compressive stress because of their high packing density, additional thermal stress may cause delamination of the films from the substrate. If film adhesion is strong enough, the high total (intrinsic plus thermal) stress might deform it. Hence, it is imperative to keep the substrates as close as possible to room temperature during deposition.

From the above, a combination of EBD and RLVIP processes (which we can run in the same coating chamber without breaking vacuum) seemed reasonable. Hardness and imperviousness to environmental contaminants (inclusive of, and primarily, water vapor) was thought to be achieved with ion plated thin films (on the outside of a multilayer stack), and stress compensation and ductility with "spongy" electron evaporated thin films. Finding the optimum combination not only of the sequence and number of the respective layers, but more so the best suited material combinations demanded substantial experimental and theoretical research. In the following, we compare the initially conceived approaches with the results achieved.

1.1. Ion-plated top and bottom (pairs of) layers, electron beam evaporated intermediate films

Rationale:

As mentioned further above, RLVIP thin films are normally very dense, hard and well adhering, but under high compressive stress and potentially brittle. Because of the latter properties and the currently still considerable heat load (although already reduced by the

heat sink measures introduced in Phase I), a multilayer coating consisting of a stack of all-RLVIP layers was unlikely to yield successful results. It is also clear from the above that a stack of all-EBD layers would likewise ill perform because of problems with density, hardness, and adhesion.

Approach:

The high vacuum coating equipment (Balzers BAP 800) available at UCF/CREOL enables both modes of operation without breaking vacuum for a typical multilayer stack consisting of nominally 2 different coating materials, e. g. SiO_2 and ZrO_2 , although normally the different processes require different starting materials for the deposition of nominally the same compound. For example, the deposition of SiO_2 thin films by RLVIP starts with the electron beam evaporation of elemental silicon which oxidizes on the surface of the substrate and the growing film. Oxygen is supplied to the coating chamber at a partial pressure of about $1 \cdot 10^{-3}$ mbar and is partially ionized by the argon plasma. The argon and oxygen ion bombardment enhances the reactivity to an extent that fully stoichiometric SiO_2 films result even from Si as the starting material.

The electron beam evaporation of SiO_2 thin films occurs from a quartz sand melt and an oxygen partial pressure closer to the 10^{-4} mbar range (of course, without an argon plasma). Similarly, the deposition of the high index layers (e. g. ZrO_2) requires also two different starting materials, so that in general up to 4 vapor sources are needed. Our BAP 800 equipment contains one electron beam evaporator with a rotating pot crucible and one somewhat larger electron beam evaporator with a 4 pocket copper crucible. Both electron guns can evaporate in a standard mode (conventional EBD) and along with the low voltage, high current plasma source which uses one crucible at a time as the anode for its discharge used in the RLVIP mode. The process control computer (DEC/PDP11) can address and index each individual pocket of the larger crucible as required by the previously determined evaporation modules of the deposition program. The thickness and deposition rate of each layer is measured with an oscillating quartz crystal monitor, which feeds its signal into the process control computer.

In this part of the program, we intended to investigate various binary combinations of the following coating materials: SiO_2 , Ta_2O_5 , TiO_2 , ZrO_2 , deposited with EBD and RLVIP.

Results:

Hampered by unfortunate extended equipment problems and the inability to further reduce the coating chamber temperature (beyond what we had basically already achieved in Phase I), we had to reduce the number of material combinations. Starting with ZrO_2 we found that our home-built chiller used for the internal water cooling of the coating chamber soon reached its capacity, and did not allow for the continuous coating of even a single layer of ZrO_2 because of the temperature rise in the coating chamber above the tolerable limit for PC lenses (see Appendices A and C). Realizing that the other two high index materials listed above, Ta_2O_5 and TiO_2 , have still a high melting point (though somewhat lower than ZrO_2), we decided to look for a high index material (oxide) that could be deposited by evaporation of a low melting metal and would easily react with oxygen upon deposition, forming a completely stoichiometric oxide as a film. Our first pick was In_2O_3 deposited in thin film form by EB evaporation of indium in a reactive oxygen atmosphere where the oxygen had been activated, ionized, and dissociated into atomic oxygen by the low voltage, high current DC plasma discharge employed for RLVIP (the activation, ionization and dissociation of O_2 supplied to the RLVIP process has been studied in an attending project using optical emission spectroscopy¹¹). Finding that In_2O_3 deposited by RLVIP seemed to behave rather nicely (both for deposition and with regard to consistent optical and mechanical properties), we adopted this material and deposition process as the standard for our further experiments in attempting to develop a durable multilayer thin film coating on plastics (PC) lenses. However, we did not fully exploit the idea of this task but went on to investigating the task following, because of the thermal problems elaborated above.

1.2. Alternating EBD and RLVIP layers

Rationale:

In this part of the program we investigated the properties of multilayer stacks deposited by alternating use of EBD and RLVIP processes, of course, again in the same coating chamber without breaking of the vacuum. The use of only two vapor sources (instead of up to four), easier design (only two different refractive indices instead of four) and programming of the deposition process, and a more continuous operation with probably shorter coating cycles was expected and considered highly desirable.

Approach:

For a typical HL multilayer stack, two options exist with several variations for the H and L layer materials (selected from the results of Part 1.1 of the program):

- a.) RLVIP for H layers, EBD for L layers
- b.) RLVIP for L layers, EBD for H layers

In both cases, this approach was to maintain the selected deposition process for a particular material for each respective layer throughout the stack. Of the two options, a.) became the process of choice, because it is normally the high index layers (refractory oxides) which grow with a columnar or granular (spongy) structure at elevated and about ambient substrate temperature, respectively, when electron beam evaporated. SiO_2 tends to form more continuous films, probably because of its intrinsic glass forming nature, though also slightly porous at low substrate temperature. EBD SiO_2 has a refractive index of about 1.45 and RLVIP refractory oxides (H layers) attain a higher refractive index than with EBD, so that this option provides for an increased refractive index contrast between H and L layers. In option b.) RLVIP SiO_2 has an refractive index of about 1.5 and EBD refractory oxides have lower refractive indices, resulting in a lower index contrast and consequently in a not as good optical performance of the respective multilayer stack.

Results:

Because of the more continuous deposition than in 1.1, we expected a better physical integrity of the completed stack. However, this assumed continuous deposition did not materialize because of the frequent interruptions during any arbitrary coating process to chill the coating chamber down to close to room temperature again.

1.3. Plasma-assisted deposition of MgF_2

Rationale:

MgF_2 is the commonly used material with the lowest refractive index available for a solid thin film material used in the visible. Its combination with any high index material will reduce the number of layers necessary to achieve a particular optical density (OD), in

comparison with SiO_2 as the low index material. As a fluoride, it should not react with the high index layers which are likely to be oxides.

Approach:

Historically, MgF_2 has been evaporated from resistance heated thermal sources (boats), as it has a rather low melting point and sufficiently high vapor pressure at the temperatures achievable with a boat to assure reasonable evaporation rates. Under these standard conditions, which include a high vacuum environment of $<10^{-5}$ mbar pressure, MgF_2 evaporates without dissociation. With the widespread use of electron beam evaporators, they have been used routinely for the evaporation of MgF_2 also; but dissociation can occur if the energy of the electron beam is too high. To investigate the feasibility of low voltage ion plating of MgF_2 , we planned to evaporate it from one of the e-beam sources available in our present equipment configuration. We expected that no reactive gas be needed if no dissociation occurred, so that the deposition would be assisted by a plain argon plasma. However, we found it more difficult than expected (when the proposal was written) to reduce the arc voltage (thought necessary to prevent dissociation of MgF_2) already under normal operational condition (regular RLVIP deposition of oxides). The complex interaction of the low voltage plasma arc with the high voltage electron beam evaporators (as shown schematically, for example, in Ref. 3) eventually prevented the realization of this proposed approach. A request to rewire the BAP 800 equipment to operate the plasma source with one of the two thermal (boat) sources available in the equipment as initially proposed was not entertained by the equipment manufacturer (Balzers), and could not be performed by ourselves because of the complexity of that system. The alternatively proposed use of a different coating equipment developed under a different contract for ion-plating-like deposition of MgF_2 did not materialize because of some hardware problems with that equipment, too.

Results:

Because of the considerations and circumstances mentioned above, we did not get to depositing MgF_2 with plasma assistance (using RLVIP or an ion-plating-like thermal evaporation process).

2. Explore transition layer between the polycarbonate substrate and the dielectric multilayer, for increased adhesion and buffering of thermal expansion mismatch

Rationale

The results achieved in Phase I show clearly that the dielectric hybrid multilayers adhered better to the polycarbonate lenses which already had a hard coating (applied by the lens manufacturer), as compared to those lenses consisting of plain polycarbonate. This is easily understandable from the nature of the hard coating, which presumably was SiO_2 -like, derived from an organo-metallic solution. Studies published earlier¹² show that such "organic" hard coatings produced by different manufacturers can result in quite different abrasion and tumble test resistance. The ideal hard coating on a plastic lens should be like hard quartz spheres (SiO_2 molecules) linked by somewhat smaller rubber-balls, which symbolize certain organic bonds. Such elastic bonds provide for good adhesion to the organic substrate material, and for increased flexibility of the hard layer, accommodating the large difference in thermal expansion of the substrate. Any hard object coming in contact with this coating, however, would see only the surface of the hard spheres, as the linking rubber balls are retracted. Such a coating would be an excellent transition layer as well, providing inorganic bonding by the hard spheres on the top, and organic bonding between the linking rubber balls and the PC substrate.

Approach

Organic Hard Coating: The development of the ideal hard coating described above was beyond the scope of our task. However, PC lenses with and without organic hard coat were tested for compatibility with both EBD and RLVIP coatings (first layers).

Plasma Polymerization: Plasma polymerization produces something like inorganic coatings from organic starting materials (monomers). In our proposal we conceived that the BAP 800 equipment might be used for such deposition experiments as well, as we had already successfully deposited hard carbon coatings, using an Ar/CH_4 mixture as a feeding gas. The analogous experiment of trying to deposit a SiO_2 containing organic layer, perhaps even with a gradual increasing content of SiO_2 toward the surface to provide a proper boundary for the subsequently following RLVIP or EBD oxide layers, did not materialize because of the hindrances caused by equipment problems etc.

mentioned above. Also, this part of the possible methods of attack was considered likely to exceed the suggested level of effort of two student-years already in our proposal (which requested about \$20,000 more funding than eventually received), and was mentioned as having little chances for success, being listed as an option which might become feasible if extraordinary progress would have been made.

Results

We found that an organic hard coating is indispensable for our deposition process, to ensure at least some level (though still unsatisfactory) of multilayer adhesion and survivability in environmental testing.

3. Expansion and refinement of heat sink installation in RLVIP coating system

Rationale

As much as the initial attempts to reduce the heat load on the plastic substrates during the coating process in the BALZERS BAP 800 chamber proved successful by introducing customized internal heat sinks, further improvement were thought to be necessary to provide for enhanced efficiency.

Approach

In Phase I, only the side chamber walls were internally water cooled. Additional water cooling has been installed in the back of the chamber (chevron) and on the inside of the front loading door. Enclosures of the evaporation sources were judged to be too impractical to even try building them, in part because of their likely interference with the high current plasma arc. The idea proposed of ultimately cooling also the substrate holder with chilled water was realized in that different coating chamber used for a different (antireflection coating on plastic lenses) project. The realization in the BAP 800 equipment was not possible because of the rotation and electrical insulation of the substrate carrier (dome). It turned out that the increased consumption of chilled water by the additional internal heat shields pushed the capacity of our home-built heat exchanger. A commercial chiller would have been needed for increased efficiency which was not available from the approved budget.

Results

Some increased cooling capacity allowed marginally the extended use of the reactive ion plating process, which generates more heat than regular electron beam evaporation, for longer deposition times (more layers). However, the expectation to eliminate extensive waiting times for chamber cool-down did not materialize, as already mentioned further above. Thus, the goal of achieving lower chamber temperatures during deposition to reduce the heat load on the plastic lenses, resulting in less thermally induced stress, did materialize only partially.

4. Investigation of structural properties and optical characterization of coatings

Rationale

The microstructure of thin films determines their optical, mechanical, and environmental durability properties to a large extent.¹³ Improvements of these properties are therefore closely tied to the detailed knowledge of the thin film microstructure as provided by electron microscope investigations¹⁴ and electron beam / ion beam microanalysis.¹⁵

Approach

We were planning to use essentially the same instruments as in Phase I, i.e. the spectrophotometer at UCF/CREOL, and transmission and scanning electron microscopes (TEM, SEM) available at the College of Engineering (UCF/COE) and also at the Major Analytical Instrumentation Center, University of Florida (UF/MAIC) in Gainesville, FL. In addition, a Scanning Auger Microprobe (SAM) had been put into operation at UCF/COE in Fall of 1990. Providing a 10% share of the equipment purchase price from a research contract on micro-metrology of optical thin films and surfaces, received in 1990 from the Florida High Technology and Industry Council (FHTIC), secures access to this useful analytical instrument.

Results

The spectral transmittance of multilayer coatings deposited on both plane glass witness samples and on actual (hard-coated) PC lenses was measured using the Perkin-Elmer 330 spectrophotometer. This instrument has been interfaced with an AT&T-type PC for data

acquisition and background subtraction. Data are stored in ASCII files that got further processed using graphing capabilities of the Microsoft Excel 4.0 spreadsheet software. Unfortunately, the accessibility of the other instruments mentioned above changed since the proposal submission. The fellow faculty member supervising the SAM fell terminally ill with leukemia and passed away this past summer. The TEM became inoperable because of age and lack of funding for a service contract. SEM investigations of highly insulating samples such as PC lenses require a more skilled operator to avoid charging and resulting ill-resolved micrographs than was available. In summary, those certainly interesting investigations could not be performed (also in part due to the reduction in the funding provided over the funding requested).

DELIVERABLES

Quarterly reports were delivered during the 2 years of this subcontract. In addition, we delivered samples at various stages of our process development. Four more samples (of the final attempt to deposit an all-RLVIP multilayer, of which 2 had been tested, and 2 are as-deposited, are enclosed with this Final Report).

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APPENDIX A

Experimental Results of All-RLVIP Multilayer Coating Deposited 9/93

A.1. Visual inspection results of salt water and humidity tests

A.1.1. Salt water test

The solution used was 5% salt (pure NaCl) dissolved in de-ionized water at room temperature.

The sample tested was #930901-10-A (ten layers of SiO_2 and In_2O_3)

Time and Date	Results
11:00 a.m. Oct. 20	Start
2:00 p.m. Oct. 20	A few cracks around particulate film defects (spatters)
5:00 p.m. Oct. 20	The cracks get bigger and some appear from other places.
11:00 p.m. Oct. 20	All the cracks get bigger.
11:00 a.m. Oct. 21	The cracks cover about one fifth of the film surface.
11:00 a.m. Oct. 21	The cracks cover about half of the film surface.

A.1.2. Humidity test

The test was performed using a Blue M humidity test chamber. Test conditions were (constant):

Relative humidity of 95%, Temperature of 49°C. Sample tested was #930901-18-A.

Time and Date	Results
2:00 p.m. Oct. 14	Start
2:00 p.m. Oct. 15	No change
2:00 p.m. Oct. 18	No change
2:00 p.m. Oct. 20	Start again
2:00 p.m. Oct. 21	No change
11:00 a.m. Oct. 22	No change initially. About 10 min. after the sample was taken from the chamber and cooled down to room temperature, cracks appeared.

From Oct. 20 to Oct. 22, the temperature in the humidity chamber was about 60°C.

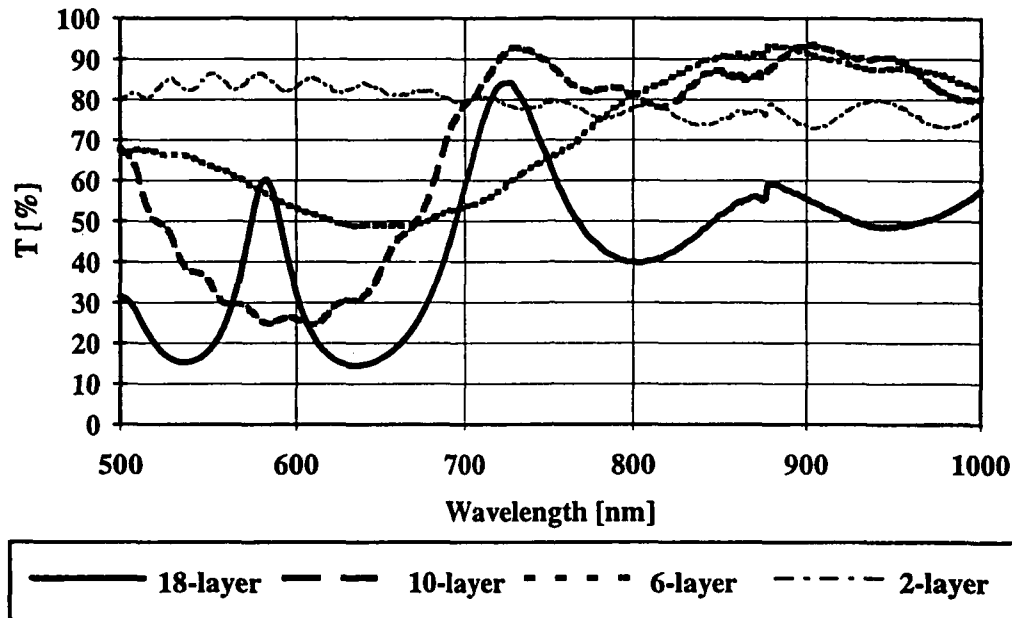
A.2. Spectral transmission measurements at several incremental layers

The environmental test results of the coatings deposited with the hybrid approach were unsatisfactory. We attributed the failure of those coatings to the "spongy" structure of the electron beam evaporated SiO_2 that was probably insufficiently "protected" by the RLVIP high index layers (In_2O_3 in most cases). Thus, during the last weeks of this Phase II project, we attempted the deposition of an all-RLVIP dielectric multilayer. To save time (which was running out) for studying the environmental durability of coatings with different numbers of layers, we applied an approach used successfully in previous laser coatings experiments because of the density and imperviousness of the RLVIP layers. While in conventional coating processes any interruption and venting of the chamber is usually strictly avoided because of uncontrolled changes of the refractive index and optical thickness due to adsorption of (moist) ambient air, such changes do not occur with RLVIP coatings because of their imperviousness.¹ Hence, we found it quite possible to interrupt a RLVIP coating process practically any time (preferably, of course, when an individual layer had been finished), vent the coating chamber, take out a substrate (for measurement of its spectral properties, for example, or for the termination of that particular coating), close the chamber, pump down, and continue the coating process with the substrates remaining in the chamber. However, this approach did not work as expected with this last coating experiment, as the spectral transmittance curves in the graph on the following page illustrate. While the coating was designed as usual for a center wavelength of 800 nm, the measured spectral transmittance (in this case measured on plane witness samples) did not match the expected (theoretical) values at all. We have not yet found out the actual reason for such grossly deviating results, and are still investigating the following possibilities:

1. Operator error in programming the BAP 800
2. Influence of the (relatively high) partial pressure of residual water vapor in the coating chamber (from out-gassing of the plastic lenses)
3. Change of vapor distribution of one or both of the electron beam evaporation sources (and consequently of the quartz crystal calibration), due to the repeated pre-melting procedure applied every time the coating process was stopped for taking out a lens.

4. Any other cause, such as some extended down-time (during the course of this experiment) because of the necessity to service (disassemble and rebuild) the rotary vane fore pump.

Spectral Transmittance of Multilayer Coatings
with different number of layers



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APPENDIX B.

Deposition of Laser Protection Lenses on Plastic Substrates

Chapter 8 of the Master's Thesis of Xiaofeng Han

1. General Considerations

The plastic lenses which we used are made of polycarbonate (PC). The transmittance band is located in range of 450 nm - 800 nm, as shown in Figure 1. The small amplitude waves on the pass band envelop are produced from a thick SiO_2 transform film ($\sim 1 \mu\text{m}$) on the plastic substrate. For those near infrared laser radiation which are generally used, such as $1.06 \mu\text{m}$ of $\text{Nd}^+:\text{YAG}$ lasers and $2.1 \mu\text{m}$ of $\text{Ho}^{3+}:\text{YAG}$ (or YFL) lasers and most of semiconductor lasers, there would be no problem, since the plastic substrates themselves can efficiently block the radiation in the near infrared region. Protecting the radiation from Ruby lasers at 694.3 nm is required. The design should be a short wave pass filter with cutoff just before 694 nm. To achieve this requirement, multilayer coatings are required.

In order to select the materials for high refractive index and low index, two factors, as follows, might be considered because of the use of plastic substrates,

- (1) the temperature should be limited below 100°C ;
- (2) the stress of the thin film should be small so that the plastic lenses would be safe.

First we thought that extra cooling water might be helpful. We installed the extra cooling pipes on the internal walls in the coating chamber. Then we would select low refractive index material and high refractive index material.

2. Selection of the Materials

(1) SiO_2 as low index material

For the low refractive index material, we used silicon dioxide (SiO_2). The design is the type of sub (HLHL...HLH) air. The layers of SiO_2 are between the high refractive index thin films. The lower the refractive index of the SiO_2 thin films is, the better it is for the fabrication because the number of total layers may be reduced. The adhesion on the

substrates and absorption of moisture from the atmosphere may not be problems. So, we used reactive electron beam evaporation for SiO_2 deposition, instead of ion plating.

The relationship of the temperature in the coating chamber with the thickness was recorded (Figure 2). For a quarter wave coating at 700 nm, the temperature was $\approx 70^\circ\text{C}$.

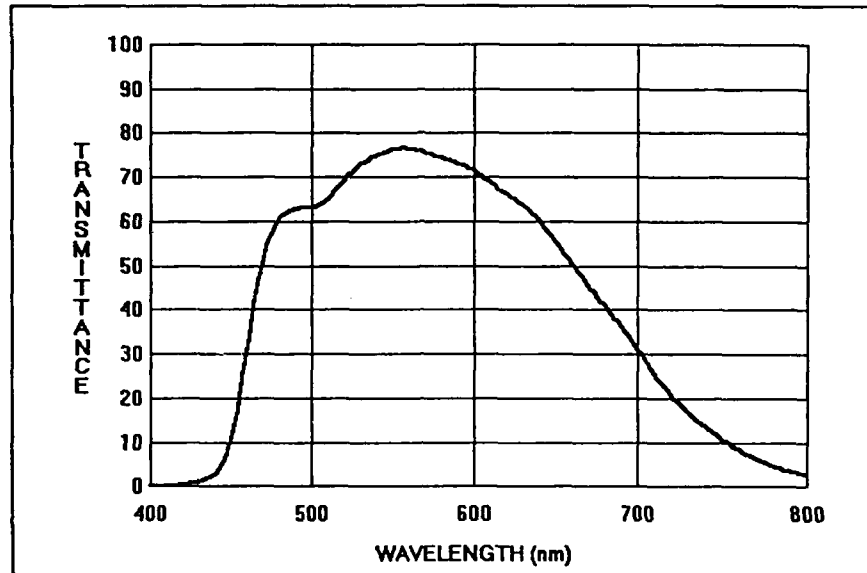


Figure 1. Transmittance of an uncoated PC lens (substrate for laser eye protection coating).

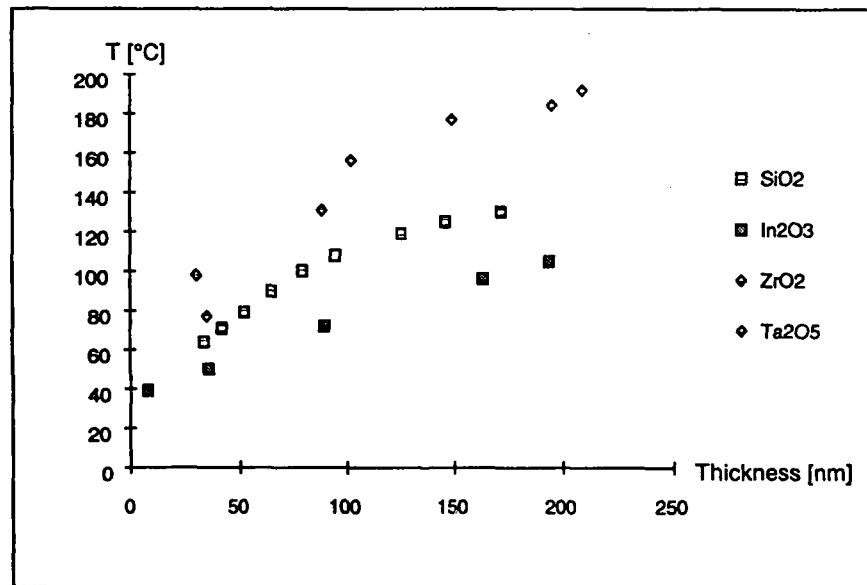


Figure 2. Dependence of the temperature in the coating chamber as a function of the physical thickness of layer materials indicated.

(2) In_2O_3 as high index material

In opposite, for high refractive index material, the higher index is, the better it is, and both top layer and bottom layer are high index films. We used reactive low voltage ion plating method for the deposition of high index material.

Normally we should first use In_2O_3 as the candidate of the high index material since the melt point of indium metal is only 156.6°C . However we thought that the melt point temperature is too low to use ion plating source because the ion beam might blast away all indium. If low power were used, the plasma might not start. However, these assumptions were wrong. Because of good thermal and electric conductivity, the temperature of the starting material, except for a small area (about 2 cm diameter) in the center of the crucible (10 cm diameter), was not high enough for evaporation at that low power. More power was needed to get 0.1 nm/sec of deposition rate. We have realized this since we started using In_2O_3 after tests of Ta_2O_5 and ZrO_2 were unsuccessful. Figure 2 shows the relationship of the temperature with thickness for In_2O_3 , ZrO_2 and Ta_2O_5 films. It can be seen that In_2O_3 deposition has the lowest temperature rise.

Even so, the temperature for a quarter wavelength thickness coating at 850 nm with In_2O_3 deposition was still up to 100°C . A quarter wavelength thickness coating had to be completed in two or three steps, that is, after completing each of 30 - 40 nm thickness coating, we stopped the process for the chamber to cool down in high vacuum.

The other three material deposits not only caused high temperature, but also lead to large stress which the plastic substrates could not stand for even multi-step coating was applied.

3. Experimental Results

First we made single layer test on plastic substrates. Figure 3 shows the transmission spectra of a single In_2O_3 film with a quarter wavelength thickness at 850 nm on the plastic substrate and the spectrum of the plastic substrate. Figure 4 gives the normalized spectrum and analog spectrum. It is clear that the lowest transmission, or high reflection, occurred at around 850, as expected.

The configuration of multilayer thin film which we used is (HLHL...H) quarter-wave stack of $\text{In}_2\text{O}_3/\text{SiO}_2$. Figure 5 shows the results of a seven-layer coating on a plastic lens.

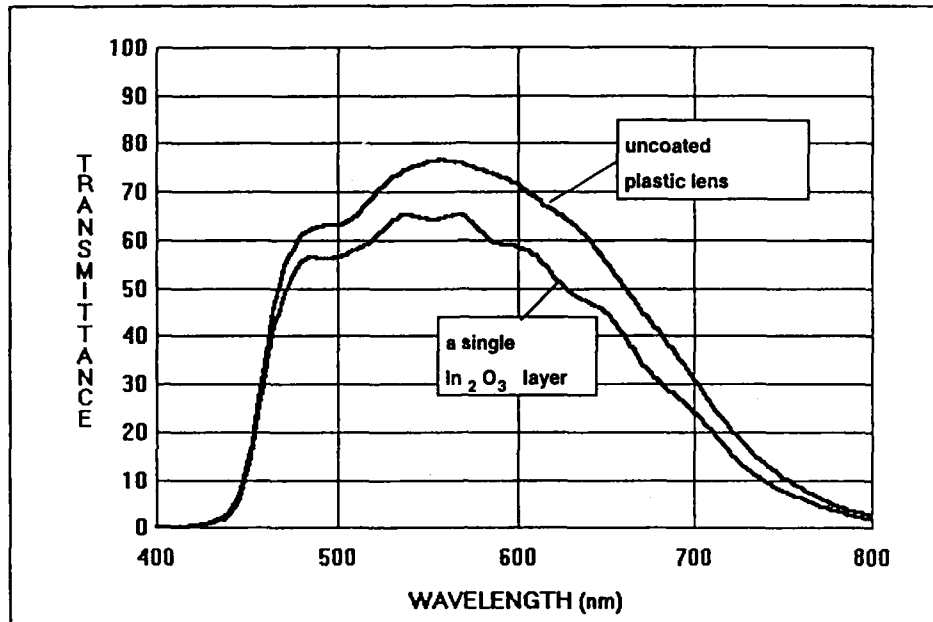


Figure 3. Transmission spectra of a single layer In_2O_3 film on plastic lens.

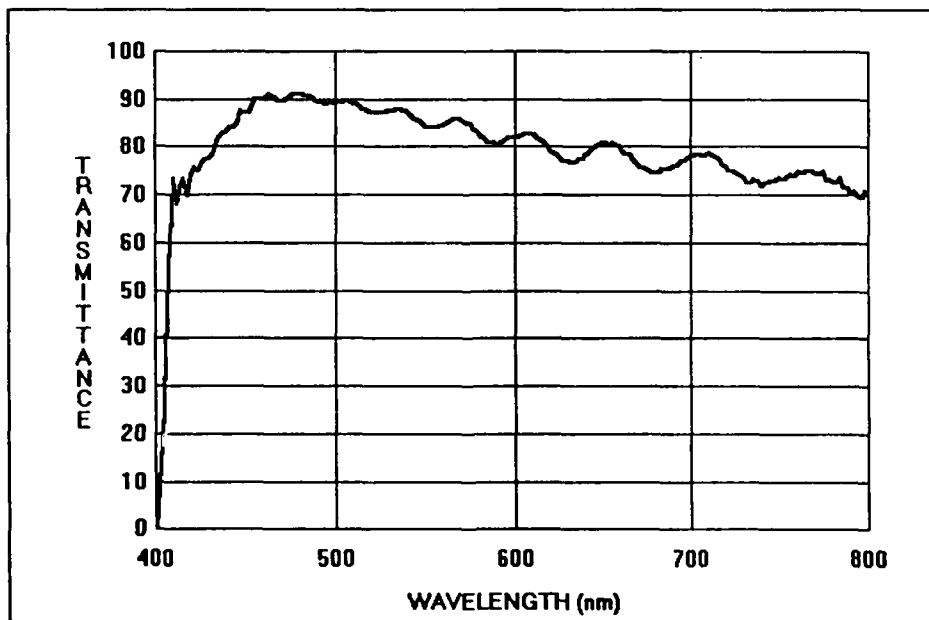


Figure 4. Normalized transmission spectrum of a single In_2O_3 layer on plastic lens.

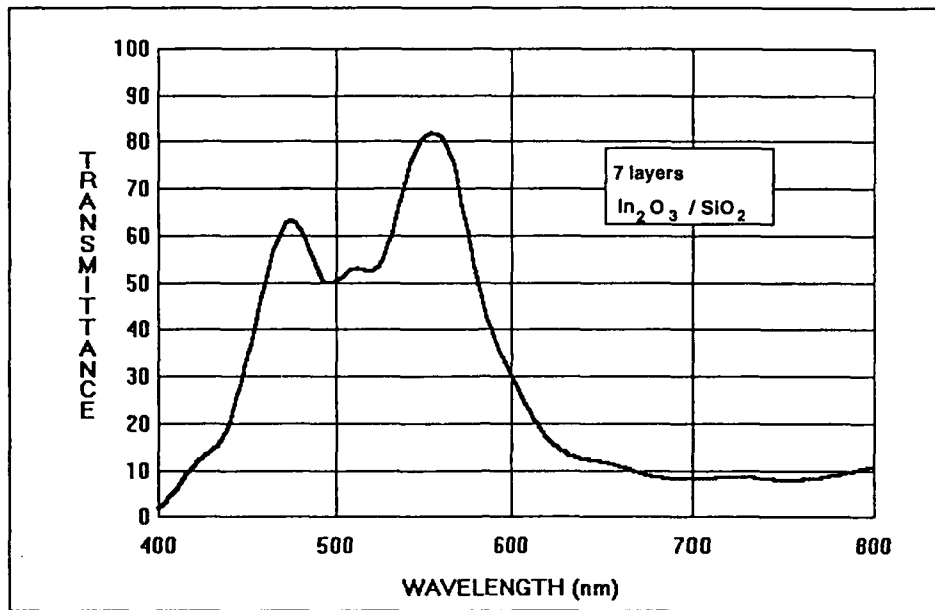


Figure 5. Transmission spectrum of a multilayer film on plastic lens.

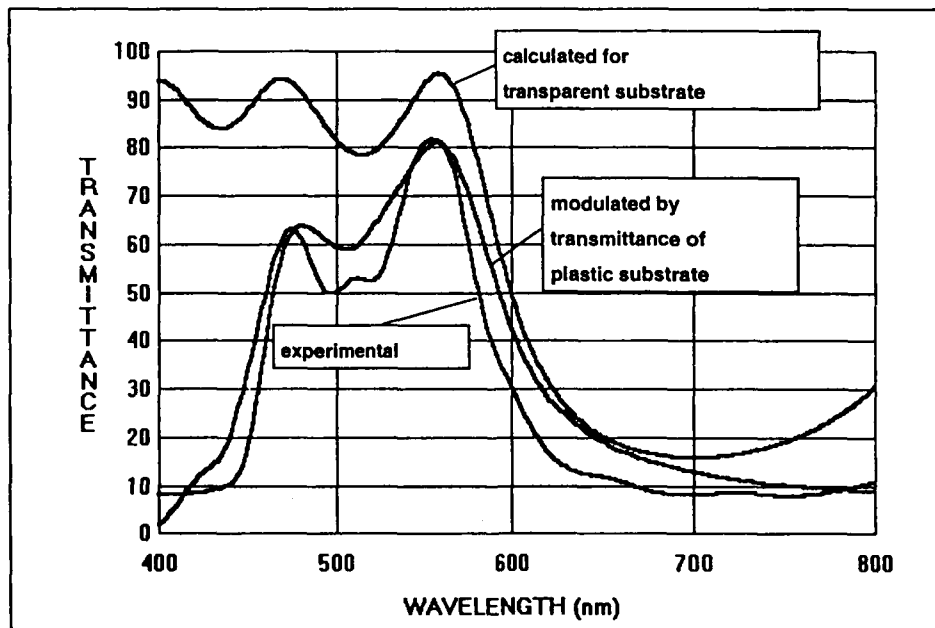


Figure 6. Calculated and experimental transmission spectra of multilayer films on plastic lenses.

4. Discussion

Figure 6 shows a comparison of the experimental result with the calculated result for the 7-layer film on the plastic lenses. The calculation used $n_H = 2.05$ and $n_L = 1.45$. The calculated result for a transparent substrate is modified by the transmittance of the plastic lenses (see Figure 1). The modified result agrees with the experimental result pretty well. However, it is hard to understand why the transmittance at 510 nm (a valley) of the experimental transmittance is ~8% lower than that of the calculated transmittance. Probably the selected parameter of high-index is lower than the real one. From our experimental result, a seven-layer thin film can reduce the transmittance down to 8% at 694 nm. This is, of course, not low enough for eye protection from a laser light beam. According to the calculation, 15-17 layer thin films are needed for obtaining 99.5% reflectance.

For the laser protecting lenses, any loss in visible of 450 nm - 650 nm is not expected. From Figure 6, we see that the loss at around 500 nm is not avoided in the quarter-wave stack design because of the large ripples. An edge filter design is required to eliminate those ripples.